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## De kristalstructuur van dibenzeenchroom

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## SUMMARY

There is a general interest in the chemical bonding in 'sandwich'  $\pi$ -complexes of transition metals with aromatic ligands. A short account on the structural features of these compounds is given in Chapter I. The structure of dibenzenechromium has been the subject of many investigations, but the results were controversial with regard to the symmetry of the benzene rings. A room-temperature X-ray diffraction study by Jellinek (1960, 1963) indicated a distortion from  $D_{6h}$  molecular symmetry; in the ligand rings carbon-carbon bonds of 1.436 (12) Å were found to alternate with bonds of 1.366 (12) Å. Another determination of the crystal structure of dibenzenechromium at room temperature was undertaken by Cotton et al. (1963). In this investigation no significant deviation from  $D_{6h}$  symmetry was observed; the length of both independent sets of C-C bonds was given as 1.387 (17) Å. Because of these contradictions we reinvestigated the crystal structure by X-ray diffraction at low temperature (100° K) in order to decrease the thermal motion which puts a serious limitation on the accuracy with which the atomic positions can be determined.

The lattice constant of the cubic crystals and the intensities were measured carefully on the Groningen manually operated three-circle diffractometer. The overall description of our experimental set-up can be found in the thesis of my co-operator Verschoor (1967). Special care was taken to decrease the unwanted background. Some constructional details on collimator and counter apertures are given in Chapter II of this thesis. It is followed by a simple discussion of the conditions on counter apertures and/or motions. It has been attempted to visualize the ideas given by Alexander and Smith (1962) and others in their detailed mathematical analyses of this problem. An analysis of the instrumental geometry in connection with the

accuracy of a lattice parameter determination is given in Chapter III. We found for the cubic crystals of dibenzenechromium  $a = 9.554 \text{ \AA}$  with an estimated standard deviation of  $0.001 \text{ \AA}$  and a possible systematic error of  $0.003 \text{ \AA}$ .

Good crystals were obtained by vacuum sublimation from the original sample of Fischer which had also been used in Jellinek's study. The crystals were covered with a very thin protecting layer of a cyanoacrylate polymer. The intensities of all 771 independent reflections up to  $(\sin \theta) / \lambda = 0.86 \text{ \AA}^{-1}$  were measured in two weeks of continuous operation. The planning of such runs is given in Table 3.5.1.  $\text{MoK}\alpha$  radiation was employed which was monochromatized by Zr-Y balanced filters. The  $\omega$ -scan technique was chosen for reasons of construction and quality of the diffractometer. Corrections were applied for the Lorentz-polarization effect, for absorption, attenuation filters, and the non-linearity and drift of the counting system. The reflections include 543 independent reflections with mixed (even and odd) indices  $hkl$ ; the Cr atoms do not contribute to the intensities of these reflections (apart from a very small contribution due to the thermal anisotropy). The intensities of 83 of these reflections were zero, 73 were just above zero, whereas 122 reflections were too weak to be measured with high accuracy. The remaining 265 independent reflections with mixed indices were used in the refinement of the structure, as were 223 independent reflections with  $h$ ,  $k$  and  $l$  all even or all odd. The strongest five reflections with unmixed indices were excluded from the refinement, since their intensities appeared to be affected by extinction. An estimate of the standard deviations in the individual structure factors was made. These can be found in the listing AANHANGSEL, and are summarized in Figure 3.8.1 (weighing according to  $1/\sigma^2$ ).

The dibenzenechromium molecule lies on a special position with symmetry  $\bar{3}$  in space group  $\text{Pa}\bar{3}$ . The positional and thermal parameters of chromium, the two carbon and the two hydrogen atoms were refined by least-squares techniques. After some isotropic cycles the hydrogen atoms were located by use of a difference synthesis. In the final cycles of the refinement, with individual weights, all atoms were assigned anisotropic thermal parameters. The result of this refinement was a hexagonal carbon ring with alternating C-C bond lengths of  $1.415$  and  $1.416 \text{ \AA}$ ; the estimated standard deviation in the difference of the C-C bond lengths is  $0.003 \text{ \AA}$ . The Cr-C bond lengths are  $2.143$  and  $2.140 \text{ \AA}$ , e.s.d.  $0.001 \text{ \AA}$ . The final

value of the index  $R$  is 0.027 for the 486 independent reflections used in the refinement and about 0.045 for all 771 independent reflections within the investigated reflection sphere. Alternative refinements in which an uniform weighing scheme and/or different scattering factor curves were used or which were done on special groups of reflections, gave essentially the same model for the molecule. It should be mentioned that rotational disorder in the crystals may obscure small distortions of the hexagonal symmetry in the individual molecules, but the results of the present study do not give any indication for such a disorder to be present. We thus conclude from our refinement that the dibenzenechromium molecules in the solid state do not show significant deviations from the symmetry  $D_{6h}$ .

An analysis of the thermal motions of the atoms is presented in terms of internal vibrations combined with translations and librations of a rigid body. There will be an apparent shortening of the bonds due to the linear representation of the thermal motions of the atoms during the refinement. For the C-C bond lengths the correction for this effect is 0.004 Å, and for C-Cr 0.005 Å.

In Chapter V a description of the crystal structure is given. This description is based on the observed molecular dimensions, combined with Van der Waals interactions between the molecules in a cubic close packing. The orientation of the molecules seems to be primarily governed by two short intermolecular H...H contacts (2.52 and 2.64 Å).

The results of the low-temperature investigation have been compared with those of the room-temperature X-ray studies. Some least-squares refinements with Cotton's and Jellinek's data, starting from our model, were performed. From Jellinek's data again a distortion of the hexagonal carbon rings was found. To check whether this is due to the restricted set of data a refinement was carried out with a low-temperature data set including the same reflections as in Jellinek's work. This time a hexagonal carbon ring was obtained, which shows that the distortion found by Jellinek may be due to inaccuracies in his data or to the fact that the correlation between the atoms increases in going from low temperature to room temperature.

The structure of dibenzenechromium has also been investigated by other experimental methods like infrared and Raman spectroscopy (Fritz et al., 1967), electron diffraction (Haaland, 1965) and neutron diffraction (Albrecht et al., 1968). At present all authors except Fritz et al., support the hexagonal symmetry of the molecule.

A survey of structure determinations of analogous compounds (Table 5.4.1) closes the thesis.